DEVELOPMENT OF NOVEL BIOSORBENTS IN REMOVING HEAVY METALS FROM AQUEOUS SOLUTION

A

Thesis Submitted

in Fulfilment of the Requirement

for the degree of

DOCTOR OF PHILOSOPHY

IN

ENVIRONMENTAL ENGINEERING

By

Md Anwar Hossain

Under the Guidance of

Prof. Dr. Huu Hao NGO

School of Civil and Environmental Engineering

Faculty of Engineering and Information Technology

University of Technology, Sydney (UTS)

Sydney, Australia

December, 2013

Certificate

I certify that this thesis has not already been submitted for any degree and is not being submitted as part of candidature for any other degree.

I also certify that the thesis has been written by me and any help that I have received in preparing this thesis, and all sources used, have been acknowledged in this thesis.

Signature of Candidate

....

(Md Anwar Hossain)

I dedicated this work to my beloved parents

Md Akbar Ali
Mosa. Ruhila Khatun

Acknowledgement

It was not simple and easy task, but both nerve-racking and enjoyable during my doctoral research at Centre for Technology in Water and Wastewater (CTWW), University of Technology, Sydney (UTS), Australia. It would not have been feasible and possible to achieve this doctoral research without the help and support of the people around me and therefore they need a special mention and thanks here.

I would like to appreciate the people for their help and support during my research. My first thanks and gratitude goes to my principal supervisor Prof. Dr. Huu Hao **NGO**. He was a source of continuous inspiration, motivation, stimulation and strength throughout my research. I would like to show my deep gratitude to my co-supervisors Dr Wenshan **GUO**, Dr. T. V. **Nguyen** and Prof. Dr. S. **Vigneswaran** for their constant help and support.

My thanks also go to lab technical officer of the environmental laboratory Md Abu Jahir and Technical officer of MEP, Mr. Harj Sandhu for their valuable effort in the environmental laboratory with appropriate instructions and methods. It is a pleasure to thank Mr. Rami Hadad, lab manager and David Hooper for their help and support. I would also like to thank my colleagues and mates Wen, Thanh, Zuthi, Hang, Zhou, Bandita, Lijuan, Santonu and Luo, I had a wonderful time with these guys.

I would like to show my gratitude to IPRS and UTS-SP authorities for the financial support to conduct this research and for living allowances to stay my family in Australia. I owe my thanks to the academic and technical support of the University of Technology, Sydney and its staff, especially Ms. Phyllis for all my academic support. Above all, I would like to thank my wife-Kabita, my children, Kabbyo and Kathon for their personal support and great patience at all times. My family was always with me during the accomplishment of this doctoral research. Thanks very much every one.

Finally, I would like to forward all my appreciation to almighty ALLAH who guided those people who supported and helped me through my research.

Table of Contents

List of Tables

Lists of Figures

Acronyms and symbols

GG	:	Garden grass
CW	:	Cabbage waste
BP	:	Banana peel
ML	:	Maple leaves
POFS	:	Palm oil fruit shells
FTIR	:	Fourier-transform infrared spectroscopy
XRD	:	X-ray diffraction
SEM	:	Scanning electron microscopy
AAS	:	Atomic absorption spectroscopy
BDST	:	Bed Depth Service Time
TEMP	:	Temperature
TIME	:	Contact time
BET	:	Brunauer, Emmer and Teller model
US EPA	:	United States Environmental Protection Agency
Cd	:	Cadmium
Cu	:	Copper
Pb	:	Lead
Zn	:	Zinc
min	:	Minute
ml	:	Millilitre (0.001 litre)
mm	:	Millimetre (0.001 metre)
l	:	Litre
MW	:	Molecular weight
A	:	Cross-section area of the media sample
C_0	:	Initial metal concentration
C_e	:	Final metal (or residual/equilibrium) concentration
m	:	Dry weight of biomass (dose)
q_e	:	Equilibrium uptake of metal
q_m	:	Maximum metal uptake or maximum adsorption capacity
V	:	Volume of liquid
K_L	:	Langmuir constant (empirical constant)
K_F	:	Freundlich capacity factor
n	:	Freundlich intensity parameter (dimensionless)
K_{RP}	:	Redlich-Peterson isotherm constant
α_{RP}	:	Redlich-Peterson isotherm constant
β	:	Redlich-Peterson isotherm exponent
A_{KC}	:	Koble-Corrigan parameter

BKC	:	Koble-Corrigan parameter
p	:	Koble-Corrigan parameter
K_T	:	Temkin isotherm constant
A	:	specific surface area
B_1	:	Temkin constant in relation to heat of sorption
b_T	:	Toth parameter
β_R	:	Radke-Prausnitz isotherm exponent
α_R	:	Radke-Prausnitz model constants
r_R	:	Radke-Prausnitz model constants
b_K	:	Khan model constant
a_K	:	Khan model exponent
S	:	Temperature dependent Unilan model constants
d	:	Temperature dependent Unilan model constants
K_{FH}	:	Flory-Huggins model's equilibrium constant
n_{FH}	:	Flory-Huggins model's exponent
B_{DR}	:	Dubinin-Radushkevich constant related to sorption energy
ε	:	Dubinin-Radushkevich polanyi potential
K_s	:	Sips isotherm constants
α_s	:	Sips isotherm constants
β	:	Sips isotherm exponent
k_1	:	First-order rate constants
k_2	:	Second-order rate constants
k_p	:	Intraparticle diffusion rate constant
K_{AV}	:	Avrami kinetic constant
n_{AV}	:	Fractionary constant for Avrami kinetic
C_s	:	The concentration at the solid/liquid interface
D	:	The axial diffusion coefficient
β_a	:	The kinetic coefficient of the external mass transfer
C_{break}	:	The outlet concentration at breakthrough
t_{break}	:	The time at breakthrough
τ	:	Time required for 50% adsorbate breakthrough
K_T	:	Thomas rate constant
θ	:	The volumetric flow rate
$\Delta G°$	:	Gibbs free energy
$\Delta H°$	:	Enthalpy change
$\Delta S°$	:	Entropy change

List of Publications

Publications and presentations as the outcomes from this study:

1. **Hossain, M.A.**, H.H. Ngo, W.S. Guo, T.V. Nguyen. "***Palm oil fruit shells as biosorbent for copper removal from water and wastewater: Experiments and sorption models***" Bioresource Technology 113 (2012) 97–101.

2. **Hossain, M.A.**, H.H. Ngo, W.S. Guo, T. Setiadi. "***Adsorption and desorption of copper(II) ions onto garden grass***". Bioresource Technology 121 (2012) 386–395.

3. **Hossain, M. A.**, H. H. Ngo, W. S. Guo and T. V. Nguyen. "***Biosorption of Cu(II) From Water by Banana Peel Based Biosorbent: Experiments and Models of Adsorption and Desorption***" Journal of Water Sustainability, Volume 2, Issue 1, March 2012, 87–104.

4. **Hossain, M. A.**, H. H. Ngo, W. S. Guo, T. V. Nguyen and S. Vigneswaran, "***Performance of cabbage and cauliflower wastes for heavy metals removal***". Journal of Desalination and Water Treatment- Science and Engineering (2013) 1–17.
5. **Hossain, M. A.**, H. Hao Ngo, W. S. Guo **"*Introductory of Microsoft Excel SOLVER function-spreadsheet method for isotherm and kinetics modelling of metals biosorption in water and wastewater*"** Journal of Water Sustainability Journal of Water Sustainability, Vol.3(4), 2013, 223–237.
6. **Hossain, M. A.**, H. Hao Ngo, W. S. Guo, J. Zhang and S. Liang. "***A laboratory study using maple leaves as a biosorbent for lead removal from aqueous solutions*".** Water Quality Research Journal of Canada (Accepted and in press).
7. **Hossain, M. A.**, H. H. Ngo, W. S. Guo, L. D. Nghiem, F. I. Hai, S. Vigneswaran, T. V. Nguyen, "***Competitive adsorption of metals on cabbage waste from multi-metal solutions*",** Bioresource Technology, (Accepted and in press).

Conference papers:

1. ***Feasibility study of palm oil fruit shells as biosorbent for copper removal from water and wastewater***, International Conference on Challenges in Environmental Science & Engineering (4th CESE 2011, Tainan, Taiwan).

2. ***Comparison study on the performance of cabbage and cauliflower for heavy metals removal***, International Conference on Challenges in Environmental Science & Engineering (5th CESE 2012, Melbourne, Australia).

Abstract

The contamination of water by toxic heavy metals including lead, cadmium, copper and zinc is a global problem. The release of these metals into the environment has become a serious health problem due to its toxicity. Progressively stricter discharge regulations on heavy metals have accelerated the search for highly efficient but economically feasible or alternative treatment methods for its removal. The use of low-cost and bio-waste or agro-waste as biosorbents for dissolved metal ions removals has shown potential to provide economic solutions to this environmental setback.

Garden grass (GG), cabbage waste (CW), banana peels (BP), maple leaves (ML) and palm oil fruit shells (POFS) have been identified as potentially low cost and efficient biosorbent for the removal of toxic heavy metals from aqueous solution. Very simple methods were used to prepare these biosorbents. The collected GG, CW, BP, ML and POFS were washed, cut into pieces, dried in oven at 105°C, grounded into powder and used for experiments.

The biosorbents were characterized by SEM, XRD, FTIR and BET tests. Surprisingly, all biosorbents showed that the surfaces of biosorbents' particles are porous, heterogeneous structures, with uneven, asymmetric steps and pores which contained high internal spaces and posed higher specific surface area. The BET surface areas are 21.28, 1.027, 22.59, 10.94 and 39.76 m^2/g for GG, CW, BP, ML and POFS, respectively. These biosorbents possesses many hydroxyl, carbonyl and phenyl functional groups (by FTIR test) and therefore, all these biosorbents are good contenders for water treatment and purification utilizations.

Biosorption of all four metals [Pb(II), Cd(II), Cu(II) and Zn(II)] by GG, CW, BP, ML and POFS was found to be dependent on experimental conditions. The optimum biosorption were noted at pH 6-6.5, shaking speed of 120 rpm, initial concentration of 10 mg/l, dose of 5g/l, contact time of 2 h and particle sizes < 75μm. The increase of temperature negatively affected the metals biosorption and at room temperature the metals biosorption process is spontaneous and exothermic in nature. The acid medium (0.1N H_2SO_4) was found be a better eluent for regeneration of exhausted biosorbents and it could be reused 5-7 times with minor deviation of efficiency except CW.

The efficient metal removing ability of biosorbents in both batch experiments and continuous flow fixed bed column bioreactors used to produce a biosorbent based metals removal system. It suggests that these novel biosorbents could lead to the development of a viable and cost-effective technology for metals removal from water and wastewaters. The prepared biosorbents were evaluated for the adsorption of Pb(II), Cd(II), Cu(II) and Zn(II) ions from single and multimetals aqueous solution by the batch method. The biosorption data were evaluated by equilibrium isotherms models. GG isotherm data posed better fitness with Langmuir, Freundlich and SIPS models as the R^2 lies between 0.991 and 0.999. Three-parameter models (Redlich-Peterson, Koble-Corrigan and SIPS) and two-parameter models (Langmuir and Freundlich) showed good fitness (R^2: 0.991-1.0) with equilibrium adsorption data from CW. The biosorption data from BP are evaluated by Langmuir, SIPS, Redlich-Peterson, Radke-Prausnitz, and Brouers-Sotolongo and results showed a good fitness as the R^2 were between 0.998 to 1. Among the models three-parameter models such as Sips, Redlich-Peterson and Unilan showed good fitness with isotherm data from ML as the R^2 are 0.988-1.00. Likewise the equilibrium data from POFS posed proper agreement with three parameter models for biosorption of Cu(II). Significantly low RMSE and χ^2 values are found from all the used models which also signify the models fitness.

The maximum Pb(II) adsorption capacities (q_m) are 54.205, 61.267, 120.096 and 50.267 mg/g for GG, CW, BP and ML respectively; whereas it were 41.66, 22.123, 50.459 and 39.599 mg/g for Cd(II) biosorption. Among the biosorbents GG, ML and POFS showed good biosorption capacities for Cu(II) ion and the values are 58.34, 34.534 and 59.502 mg/g. The Zn(II) adsorption capacities are moderate and the magnitude of capacities are 57.53, 12.236, 51.896 and 29.94 mg/g for GG, CW, BP and ML respectively. A strong antagonisms were found among the metals ions [Pb(II), Cd(II), Cu(II) and Zn(II) ions] in the multimetals adsorption systems though Pb(II) and Cd(II) ions dominated. Surprisingly, the maximum reduction in capacities were also found for Pb(II) and Cd(II). The equilibrium and kinetics data for desorption were also evaluated the by isotherm models and kinetics models. Some data from GG and ML showed good agreement with models but most of the data did not pose appropriate fitness.

The kinetics of metal removal by all biosorbents was extremely fast, reaching equilibrium in about 15-60 minutes which is showed the practical potentiality. The both pseudo-first-order and pseudo-second-order models was found to be the best fit (R^2: 0.991-1.00) to describe the biosorption mechanism of Pb(II), Cd(II), Cu(II) and Zn(II) ions onto the biosorbents. This is implies that the adsorption mechanisms are both physisorption and chemisorption. As reaction constant, k_2 and n_{AV} (from order and Avrami equation) values were greater than 1 suggested that biosorption reaction is more than one order. Intraparticle diffusion also involved for biosorption process. Along with this, Elovich and Fraction power models also posed good fitness with kinetics data.

The metal removing capacity of CW was also tested in continuous flow fixed-bed column bioreactors for artificial wastewater. The removal capacities were 15.72, 62.23, 68.23 and 70.71 times higher than that obtained in a batch system for Pb(II), Cd(II), Cu(II) and Zn(II) ions. The appropriate service times to breakthrough and metals ions concentration were 5-10 h and 10 mg/l, respectively. The design of a continuous fixed bed column treatment system with CW biosorbent for Pb(II), Cd(II), Cu(II) and Zn(II) laden wastewater can be reached using the BDST, Yoon-Nelson and Clark breakthrough models.

Elucidate the biosorption mechanisms is one of the aims for biosorption of metals. Fitness of pseudo-first-order and pseudo-second-order models suggested the biosorption are both physisorption and chemisorption. FTIR tests showed the functional groups which responsible ions exchange. Isotherm data fitted more with three-parameter models which signifies the adsorption onto heterogeneous surface. It is also found from SEM and XRD data. Thus, it could not be ascertained from the results which single mechanism involved for metals biosorption. However, it could presume that combination of all mechanisms with complexation are responsible for Pb(II), Cd(II), Cu(II) and Zn(II) ions and therefore, high biosorption capacities were found.